

UNITED STATES PATENT APPLICATION

OF

**THOMAS H. BAUM
PHILLIP CHEN
FRANK DIMEO, JR.
PETER C. VAN BUSKIRK
PETER S. KIRLIN**

FOR

PLASMA-ASSISTED DRY ETCHING OF NOBLE METAL-BASED MATERIALS

GOVERNMENT RIGHTS IN INVENTION

[0001] Some aspects of this invention were made in the performance of U.S. Government Contract No. DDALO1-97-C-0079, "BST Capacitors for Cryogenic Focal Plane Arrays;" NIST ATP Program, 70NANB9H3018. The U.S. Government has certain rights in the invention hereof.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This application is a continuation-in-part of co-pending U.S. Application No. 09/453,995, filed on December 3, 1999, which is a continuation-in part of U.S. Application No. 08/966,797, filed on November 10, 1997 and issued on January 25, 2000 as U.S. Patent No. 6,018,065; and a continuation-in-part of co-pending U.S. Application No. 09/093,291, filed on July 8, 1998.

BACKGROUND OF THE INVENTION

Field of the Invention

[0003] The present invention generally relates to a process for removal of noble metal-based materials, and more particularly in a preferred aspect to "dry" etching of deposited iridium-based materials to fabricate microelectronic device structures.

Description of the Related Art

[0004] Iridium (Ir) and iridium oxide (IrO₂) are of great interest for use as electrode materials in both dynamic random access memories (DRAMs) and for ferroelectric-based memory devices (e.g., FRAMs) that incorporate perovskite metal oxide thin-films as the capacitor layer.

[0005] The advantages of Ir over other possible electrode materials include ease of deposition, e.g., using chemical vapor deposition (CVD), the ability to “dry” etch the material, the ability to form a stable conducting oxide (IrO_2) at high temperatures in an oxidizing environment, the ability to convert IrO_2 back to Ir metal at suitable temperatures (on the order of 350°C) in forming gas, and the ability of the corresponding product microelectronic device to operate stably at high temperatures with a high degree of reliability.

[0006] The deposition and/or processing of Ir-based electrodes is highly desirable based on the above-discussed advantages. Ir displays a resistivity 5.3×10^{-5} -cm at 20°C and IrO_2 is highly conducting with a reported resistivity of 100×10^{-5} -cm. The formation of IrO_2 occurs only at elevated temperatures ($>550^\circ\text{C}$) in O_2 and is a superior material for the deposition of complex oxides for dielectric or ferroelectric capacitors. Further, during the high temperature CVD process for the growth of these capacitors, the formation of IrO_2 can be advantageous for limiting inter-diffusion, as for example by acting as a diffusion barrier to oxidation of conducting polysilicon vias or plugs. IrO_2 therefore is a material having many advantages in forming a robust, low-leakage electrode for reliable device fabrication.

[0007] Based on the need for Ir-based electrodes, a facile etching method for Ir is critical for commercial manufacturing processes, particularly those involving CVD techniques, since CVD enables the fabrication of electrode structures having dimensional characteristics below 0.5 micron.

[0008] In order to obtain useful electrode structures, it generally is necessary to etch the deposited Ir-based material, to form elements of a desired dimensional and locational character. Heretofore, “dry” etching techniques utilizing plasma for reactive ion etching

(RIE) have been generally chlorine-based and resulted in significant residue being left on the structure after completion of the etching process.

[0009] Depending on the type of structure being formed, such post-etch residue can result in short circuiting, undesirable topography and/or other deficiencies in the subsequent operation of the product microelectronic device. Prevention of the formation of such residues can be achieved in some instances by manipulating the reactive ion etching (RIE) process parameters, but such process manipulation produces undesirable sidewall slopes in the microelectronic device structure that in turn prevent useful submicron capacitors from being fabricated from iridium-based materials.

[0010] Accordingly, it would be a significant advance in the art of fabricating microelectronic devices and precursor structures therefor, to provide a simple and commercially useful “dry” etch methodology applicable to Ir-based materials that provides high etching rates, superior etching uniformity and effective control over the shape of the etched features.

SUMMARY OF THE INVENTION

[0011] The present invention relates in one aspect to a method for removing residue from or “dry” etching a noble metal material previously deposited on a substrate, such as a microelectronic device, by contacting the deposited material with a gas-phase composition comprising at least one energized halogenated organic and/or inorganic compound or mixture thereof, thereby etching or removing the deposited material to yield a desired structure formed of the noble metal material, e.g., an electrode or other structural component or feature of a microelectronic device.

[0012] The gas-phase composition or plasma contacting is advantageously carried out in an "oxidizing ambient environment" for a sufficient time and under sufficient conditions to effectively etch the deposited noble metal material or remove noble metal residue, thereby reducing deficiencies in the operation of the microelectronic device.

[0013] The method of the present invention is usefully employed for etching or removing noble metal materials including, without limitation, platinum, palladium, iridium, rhodium and materials comprising alloys or combinations of such metals, as well as alloys or combinations of one or more of such metals with other (non-noble) metal. Most preferably, the noble metal material is an iridium-based material.

[0014] As used herein, the term "Ir-based" or "iridium-based" refers broadly to elemental iridium, iridium oxide and iridium-containing material compositions including iridium alloys. As used herein, the term "microelectronic device structure" refers to a microelectronic device, or a precursor structure that must be subjected to subsequent processing or treatment steps to fabricate a final product device.

[0015] As used herein, the term "dry" etch refers to etching that is carried out using gaseous reagents, as opposed to wet-etching methods in which liquid-phase reagents are employed to effect material removal from a deposited metal thin film, or layer of material. The "dry" etch process of the present invention is a plasma etching process. A "plasma" is a highly ionized gas with a nearly equal number of positive and negative charged particles plus free radicals. The free radicals are electrically neutral atomic or molecular species that can actively form chemical bonds.

[0016] In the plasma etching process or residue removal process of the present invention, free radicals generated in a plasma and acting as a reactive species, chemically combine with materials to be etched or removed and form volatile compounds that are readily removable from the system, e.g., by an evacuating device joined in closed flow communication with the plasma etch chamber.

[0017] The reactive etching reagent may include, for example, at least one halogenated compound selected from an organic halogenated compound, such as C_2F_6 ; inorganic halogenated compound, such as XeF_2 and SF_6 or a mixture of halogenated organic and inorganic compounds, such as C_2F_6 and XeF_2 , and an oxidizing gas to a sufficient amount of energy to generate reactive species sufficiently energized to etch the deposited iridium-based material upon contact therewith.

[0018] The halogenated organic compounds that are useful as "starting material" for plasma generation to form the etching medium, can comprise any compound that will effectively provide, upon energizing, a reactive halogenated etching gas. Suitable halogenated organic compounds useful in specific applications of the plasma etching process include, without limitation, alkyl halides having an alkyl moiety selected from C_1 - C_6 alkyl species, with at least some and preferably all of the hydrogen substituents of the alkyl moiety being replaced by halogen. Specific examples of alkyl halides include, without limitation, CF_4 , C_2F_6 , $C_2Cl_3F_3$, C_4F_8 , C_5F_8 , C_3F_8 , $C_2Cl_2F_4$, C_2ClF_3 , $CClF_3$, CCl_3F , CCl_2F_2 , etc., with C_2F_6 being a particularly preferred alkyl halide species. The halogenated organic compound can include any suitable halogen substituent, e.g., fluorine, bromine, chlorine, or iodine, with fluorine generally being the most preferred.

[0019] In one aspect, an etching gas mixture is employed for the etching of the noble metal-based material, in which the etching gas mixture includes (i) at least one halogenated

organic compound and (ii) at least one gas that provides an "oxidizing ambient environment" to assist in the volatilization and removal of iridium product species from the iridium-based material on the substrate.

[0020] As used herein, the term "oxidizing ambient environment" means an environment including oxygen-containing gas, such as oxygen (O₂), ozone (O₃), air, nitrogen oxide (NO), nitrous oxide (N₂O), carbon monoxide (CO) or the like, and preferably O₂. Such oxidizing atmosphere may be provided in a processing chamber with the introduction of the halogenated organic compound into the chamber to effect the etching of the noble metal-based material.

[0021] In one specific embodiment of the dry plasma etching process, the product etched structure, such as for example an electrode or other component of a microelectronic device, is formed with a microwave or radio frequency (RF)-generated etching plasma. Any suitable RF or microwave radiation may be used for plasma generation. In one embodiment of such process, the halogenated compound(s), in an oxidizing ambient environment, is energized in a RF-processing system to produce the plasma for the etch operation.

[0022] In another embodiment of the present invention, the product etched structure is formed with a microwave-generated etching plasma. Any suitable microwave radiation may be used for plasma generation.

[0023] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF

[0024] The present invention is based on the discovery that noble metal-based materials, e.g., iridium, platinum, palladium, and rhodium and based electrode structures, can be readily formed into a desired configuration by employing a “dry” etch processing technique on the noble metal-based material, e.g., by utilizing reactive etching gases comprising halogenated organic and/or inorganic compounds in an oxidizing ambient environment.

[0025] While the ensuing discussion herein is sometimes hereinafter directed illustratively to iridium as the noble metal forming the deposit to be etchingly altered, it will be appreciated that the invention is not thus limited in utility, but that the invention contemplates plasma etching generally of noble metal-based materials, of which iridium is a widely used species for fabrication of electrodes and other conductive elements and features of microelectronic device articles and precursor structures.

[0026] Accordingly, with reference to iridium as a noble metal species illustrative of the method of the invention, the iridium initially can be deposited on the substrate in any suitable manner, including chemical vapor deposition, liquid delivery, sputtering, ablation, or any other suitable technique known in the art for deposition of such metal on a substrate from a metal organic or other precursor or source material. Among the foregoing techniques, chemical vapor deposition is preferred when the iridium-based structures to be formed have critical dimensions below about 0.5 microns. In the deposition of Ir-based materials on a substrate by chemical deposition methods, the precursor for the chemical vapor deposition of the iridium component may be any suitable iridium precursor compound, complex, or composition that is advantageous for yielding iridium during the deposition process.

[0027] Prior to contacting of the deposited noble metal-based material on the substrate, the noble metal may be masked, or patterned, e.g., by conventional photoresist or other patterning technique(s), to form a lithographically or otherwise defined pattern for subsequent etch processing.

[0028] Etching of the deposited Ir-based material is carried out by contacting the deposited iridium-based material with a reactive etching reagent. The reactive etching reagent may include, for example, at least one halogenated compound selected from an organic halogenated compound, such as C_2F_6 ; inorganic halogenated compound, such as XeF_2 and SF_6 or a mixture of halogenated organic and inorganic compounds, such as C_2F_6 and XeF_2 , and an oxidizing gas to a sufficient amount of energy to generate reactive species sufficiently energized to etch the deposited iridium-based material upon contact therewith. The contacting of the deposited Ir-based material with the reactive species is carried out for a sufficient time and under sufficient conditions to form an etched surface structure of the desired configuration.

[0029] The dry clean process of the present invention may be carried out at any suitable process conditions, including ambient temperature, low temperature and elevated temperature regimes, as well as varying pressure regimes. For example, the cleaning process may be carried out at room temperature conditions involving the sublimation of XeF_2 to generate same as an active cleaning agent. XeF_2 may also be first reacted with another compound, such as silicon, to generate an active cleaning agent comprising SiF_2 radicals.

[0030] The time and contacting conditions for the reactive halide etch process may be readily determined by those of ordinary skill in the art. The nature and extent of the etching of the deposited noble metal-based material may be empirically determined while

varying the time and/or contacting conditions (such as temperature, pressure, and concentration (partial pressure) of the etching agent to identify the process conditions producing a desired etching result.

[0031] The halogenated organic compound can comprise any compound that will effectively provide, upon energizing, a reactive halogenated etching gas. The halogenated organic compound can include, for example, one or more alkyl halides, e.g., C₁-C₆ alkyl halides such as CF₄, C₂F₆, C₂Cl₃F₃, C₄F₈, C₅F₈, C₃F₈, C₂Cl₂F₄, C₂ClF₃, CClF₃, CCl₃F, CCl₂F₂, etc., with C₂F₆ being highly preferred as a source halocompound to form the etching medium. The halogenated organic compound may comprise any suitable halogen substituent(s), e.g., fluorine, bromine, chlorine, and/or iodine, with fluorine generally being the most preferred. The halogenated organic compound may be partially or fully halogenated, with fully (halo)substituted compounds being preferred, and perfluorocompounds being most preferred.

[0032] Advantageously, especially in the case of iridium and/or iridium oxide as the noble metal on the substrate, the etching gas mixture includes the halogenated organic compound in combination with at least one oxygen-containing gas, to assist in the volatilization and removal of iridium product species from the iridium-based material on the substrate. The oxygen-containing gas may include, for example, one or more of O₂, O₃, N₂O, CO, NO, etc. Preferably, the oxygen-containing gas is O₂, O₃ or a mixture thereof.

[0033] While not wishing to be bound by any specific theory of operation, it is believed that the inclusion of an oxygen-containing gas may be advantageous with the use of halogenated organic compounds, to reduce the amount of free carbon available (by reaction of carbonaceous species with the oxygen-containing gas to form CO and CO₂).

This substantially prevents any formed polymeric by-products from depositing on the interior surface of the chamber or the etched surfaces. Additionally, any formed CO gas is available to increase etch rates; for example, in applications where the halo species, X = chlorine or bromine, the presence of CO gas serves to enhance the reactant volatility through the formation of $(\text{CO})_y\text{IrX}_3$ and $\text{Ir}(\text{Cl})_4$.

[0034] The source gas mixture for the etchant medium therefore comprises a halogenated organic compound, e.g., C_2F_6 , and an oxidizing gas, e.g., O_2 , and may be energized in any suitable manner, such as in a RF or microwave processing system.

[0035] There are two fundamental types of microwave plasma processing systems, the oven type and the downstream type. The oven type microwave plasma processing system provides a single chamber wherein the plasma generating and reacting regions are combined. The article to be etched is placed in the single chamber and exposed not only to the generated plasma but also to the radiation source. Alternatively, and preferably, a downstream type of microwave plasma processing system, having separated generating and reaction regions, is employed, wherein the workpiece is placed outside of the plasma generating region in the downstream reacting region. This downstream processing type of microwave plasma processing system is preferred because the workpiece is not exposed to the electromagnetic radiation necessary to energize the etching gases.

[0036] Owing to the fact that downstream microwave plasma processing is preferred in the general practice of the invention when microwave energization of the source gas(es) is employed for plasma formation, the ensuing description in respect of plasma processing refers to the preferred downstream microwave processing.

[0037] In the plasma processing system, the illustrative reactive gas mixture of C_2F_6 and O_2 , whose components may be added either simultaneously or separately to the process chamber, is introduced to the plasma generating chamber and ionized by microwave to form a plasma. The continuous volumetric flow ratio of C_2F_6 to O_2 in such process can for example be on the order of from about 100 to about 0.1, and more preferably from about 4 to about 0.5.

[0038] Radicals generated in the plasma generating region of the microwave processing chamber are subsequently introduced into the reacting region of the processing chamber to react with the Ir-based material. The distance between the generating and reacting region may be varied depending on the etch requirements and the specific system variables involved. By way of illustration, such distance may for example be on the order of from about 8 mm to about 600 mm dependent on the active life of the radicals.

[0039] Some radicals are long-lived and are capable of surviving many collisions (with other particles and the walls of the chamber) while maintaining sufficient energy to reach the reacting region. Other radicals are not as stable, and as such decay before reaching the reacting region. As a result, when using a mixture of gases containing both long- and short-lived radicals, the distance between the generating and reacting regions will desirably be adjusted accordingly. Advantageously, in the present invention, the use of C_2F_6 as a source material for the etchant medium tends to extend the active life of the O_2 radicals, thereby accommodating the provision of a moderate distance between the generating and reacting regions, e.g., a spacing distance in the range of from about 150 mm to about 600 mm.

[0040] In the microwave processing system, the plasma is typically generated in the preferred gas mixture of C_2F_6 and O_2 at a pressure in the range of from about 0.005 Torr to

about 2 Torr by electromagnetic radiation having a frequency in the range of from about 1×10^8 Hz to about 1×10^{12} Hz.

[0041] If an RF processing system is utilized, the plasma is typically generated by electromagnetic radiation having a frequency in the range of from about 1×10^3 Hz to about 1×10^{12} Hz, more preferably in a range from about 1×10^5 Hz to about 1×10^8 Hz, and most preferably, the electromagnetic radiation is about 400 KHz.

[0042] The process gas mixture and processing conditions required to etch the Ir-based material typically depend on the etching features and shape of the product structure. The time and contacting conditions advantageously employed in a specific end use application of the invention may be readily determined by those of ordinary skill in the art, by the simple expedient of empirical determination of the etching of the deposited Ir-based (or other noble metal-based) material while varying the time and/or contacting conditions such as temperature, pressure, concentration of the etching agent, etc., to provide the desired results.

[0043] Generally, the process gas mixture comprising C_2F_6 and O_2 gases is introduced into the plasma processing system continuously at a suitable flow rate to maintain a continuous source of energized radicals. Typically, a suitable flow rate for the introduction of the gases into the plasma generating region ranges from about 200 sccm to about 1000 sccm, however, actual flow rates will be dependent on the volume of the reactor chamber and as such the above flow rates are illustrative only, and are not to be limitingly construed.

[0044] During the etching process, the Ir-based substrate may suitably be maintained at an appropriate temperature, e.g., a temperature ranging from about 0°C to about 100°C, and more preferably from about 20°C to about 50°C.

[0045] The plasma energized halogenated organic compounds may further comprise the reaction product of an initial reaction, e.g., reacting C₂F₆ with O₂ to form COF₂.

[0046] In one embodiment, at least one halogenated compound selected from an organic compound, such as C₂F₆; inorganic halogenated compound, such as XeF₂, SF₆; SiF₄, Si₂F₆, Si₂OF₆, and radicals SiF₂ and SiF₃; or mixture of halogenated organic and inorganic compounds, such as C₂F₆ and XeF₂ may be used as a gas-phase reactive halide composition or an etching gas to assist in the volatilization and removal of a noble metal, such as an iridium species from an iridium-based material deposited on a substrate.

[0047] In another embodiment, at least one halogenated compound selected from an organic halogenated compound, such as C₂F₆; inorganic halogenated compound, such as XeF₂ and SF₆ or a mixture of halogenated organic and inorganic compounds, such as C₂F₆ and XeF₂ may be used as an etching gas wherein the halogenated compound is reacted with elemental silicon or quartz substrates in the presence of O₂ or O₃, and the resultant active products, including for example, SiF₄, Si₂F₆, Si₂OF₆, and radicals SiF₂ and SiF₃, may be used as an etching gas, to assist in the volatilization and removal of iridium species from the iridium-based material on the substrate. Radicals SiF₂ and SiF₃ may further be generated by passing SiF₄ through an energetic dissociation source, wherein the energetic dissociation source is selected from the group consisting of a plasma source, an ion source, an ultra violet source and a laser source.

[0048] Preferably, the etching gas compositions lack nitrogen-and/or phosphorous-containing compounds, such as nitrogen- and/or phosphorous-containing σ -acceptor ligands to prevent interaction of the σ -acceptor ligands with the silicon or etching surface. When the silicon-containing active species are generated by interaction with the halogenated organic and/or inorganic compounds during the etching process, it is believed that highly volatilized iridium species are formed that may include iridium-silicon halide complexes that are generally described as IrX_1 , IrX_3 , IrX_4 and/or IrX_6 (where X = silicon halide complex), and more specifically $\text{Ir}(\text{SiF}_2)_x$, where $x = 1, 2, 3$ or 4 , such as IrSi_2F_4 , IrSi_3F_6 and/or IrSi_4F_6 . It is believed that if the etching composition comprises nitrogen-and/or phosphorous-containing species, such as nitrogen-and/or phosphorous-containing σ -acceptor ligands, that are in proximity to the etching surface the nitrogen-and/or phosphorous-containing species will interact with other components in the composition or with the resultant volatilized species and reduce the effectiveness of the etching or the volatility of the volatilized species.

[0049] In another aspect of the invention, iridium may be removed from a microelectronic device structure by contacting the microelectronic device structure with a gas-phase reactive halide comprising XeF_2 and an agent to assist in volatilizing, such as a Lewis-based adduct or electron back-bonding species. The agent is selected from the group consisting of carbon monoxide, trifluorophosphine, and trialkylphosphines to accelerate the rate of etching by enhancing the volatility of the etch by-products and noble metal (halide) $_x$ species or noble metal (halide radical) $_x$ species.

[0050] The microelectronic device structure is contacted with the reactive halide and agent for a sufficient time to at least partially removing the iridium metal residue from the microelectronic device structure.

[0051] In yet another aspect of the invention, the iridium-containing film prior to its formation, as an electrode structure, may have deposited thereon a high temperature dielectric and/or ferroelectric material. This is usually accomplished in an oxidizing environment. As such the oxidizing ambient environment may be employed not only during deposition of the oxide dielectric/ferroelectric, but may also be used during the subsequent etching process for forming the electrode structure.

[0052] In addition to the etching of a deposited Ir-based material as an Ir-based electrode structure, it is contemplated that etching processes in accordance with the present invention may be used to clean an Ir CVD chamber to reduce particle formation and contamination therein.

[0053] The etching methods of the present invention may also be employed in etching Ir-based material deposited on or over a high temperature dielectric material or ferroelectric material, so that the Ir-based material serves as a top electrode structural material, as well as a hard mask layer to pattern the underlying dielectric or ferroelectric material.

[0054] The dielectric or ferroelectric material may comprise any suitable material for the specific end use or application being contemplated. Examples of potentially useful materials include SBT, PZT, BST, PLZT, PNZT, and LaCaMnO₃.

[0055] The etching methods of the present invention may be utilized for iridium films deposited for the formation of electrode and other elements of semiconductor devices, such as for example DRAMs, FRAMs, hybrid systems, smart cards and communication

systems, as well as any other applications in which the thin films of iridium and/or iridium oxide, or combinations thereof, are advantageously employed.

[0056] The features and advantages of the invention are more fully shown by the following non-limiting example. This example illustrates one embodiment of the present invention involving etching of Ir-based materials deposited on a substrate to form Ir-based material structures thereon. As discussed hereinabove, methods in accordance with the present invention may be usefully employed to form etched metal structures deriving from a variety of noble metal-based materials.

EXAMPLE 1

[0057] An Ir-based material layer approximately 40 nm thick was deposited on a quartz crystal microbalance disk and placed on a support in the reacting chamber of a downstream microwave processing system.

[0058] A mixture of process gases including C_2F_6 and O_2 in a volumetric flow ratio (such ratio being a dimensionless value, wherein the volumetric flow rate of each of the respective halocarbon and oxidant gases is measured in the same units, e.g., of standard $ft^3/minute$) of 1 was continuously introduced into the microwave plasma generating region at a flow rate of approximately 1,100 sccm.

[0059] A plasma was formed from the process gases using a microwave plasma generator and the resultant plasma then was introduced into the reacting region of the plasma system. The etching process was performed for approximately 25 minutes, which was a sufficient time to completely remove the Ir-based material from the quartz crystal microbalance substrate.

[0060] While the invention has been described herein with reference to specific features, aspects and embodiments, it will be recognized that the invention may be widely varied, and that numerous other variations, modifications and other embodiments will readily suggest themselves to those of ordinary skill in the art. Accordingly, the ensuing claims are to be broadly construed, as encompassing all such other variations, modifications and other embodiments, within their spirit and scope.